

NATO LECTURES

M. Meyyappan

Nanotechnology in Aerospace Applications

Abstract

The aerospace applications for nanotechnology include high strength, low weight composites, improved electronics and displays with low power consumption, variety of physical sensors, multifunctional materials with embedded sensors, large surface area materials and novel filters and membranes for air purification, nanomaterials in tires and brakes and numerous others. This lecture will introduce nanomaterials particularly carbon nanotubes, and discuss their properties. The status of composite preparation – polymer matrix, ceramic matrix and metal matrix – will be presented. Examples of current developments in the above application areas, particularly physical sensors, actuators, nanoelectromechanical systems etc. will be presented to show what the aerospace industry can expect from the field of nanotechnology.

Of all the nanoscale materials, carbon nanotubes (CNTs) have received the most attention across the world. These are configurationally equivalent to a two-dimensional graphene sheet rolled up into a tubular structure. With only one wall in the cylinder, the structure is called a single-walled carbon nanotube (SWCNT). The structure that looks like a concentric set of cylinders with a constant interlayer separation of 0.34 Å is called a multiwalled carbon nanotube (MWCNT).

The CNT's structure is characterized by a chiral vector (m, n) . When $m-n/3$ is an integer, the resulting structure is metallic; otherwise, it is a semiconducting nanotube. This is a very unique electronic property that has excited the physics and device community

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leading to numerous possibilities in nanoelectronics. CNTs also exhibit extraordinary mechanical properties. The Young's modulus is over 1 TPa and the tensile strength is about 200 GPa. The thermal conductivity can be as high as 3000 W/mK. With an ideal aspect ratio, small tip radius of curvature and good emission properties, CNTs also have proved to be excellent candidates for field emission. CNTs can be chemically functionalized, i.e. it is possible to attach a variety of atomic and molecular groups to the ends of sidewalls of the nanotubes.

The impressive properties alluded above have led to investigations of various applications. The most important aerospace application is high strength, low weight composites. Investigation of metal and ceramic matrix composites with CNTs as a constituent materials is in its infancy. A status update will be provided. CNTs have been shown to provide desirable electrical properties for polymer matrix composites. In many cases, the current problem is the inability to disperse the nanotubes homogeneously across the host matrix.

Other applications for CNTs include electronic components, logic and memory chips, sensors, catalyst support, adsorption media, actuators, etc. All early works in nanoelectronics use CNTs as a conducting channel in an otherwise silicon CMOS configuration. This approach may not really have a future as the use of CNTs, while inherently not solving any of the serious problems of CMOS downscaling (such as lithography, heat dissipation, etc.), it doesn't show an order of magnitude performance improvement either. The critical issue now is to develop alternative architectures in addition to novel materials. In contrast, the opportunities for CNTs in sensors – both physical and chemical sensors – are better and near-term.

The opportunities for aerospace industry are through thermal barrier and wear resistant coatings, sensors that can perform at high temperature and other physical and chemical sensors, sensors that can perform safety inspection cost effectively, quickly, and efficiently than the present procedures, composites, wear resistant tires, improved avionics, satellite, communication and radar technologies.

Nanotechnology: Aerospace Applications

M. Meyyappan

Nanotechnology Areas of Interest to Aerospace Community

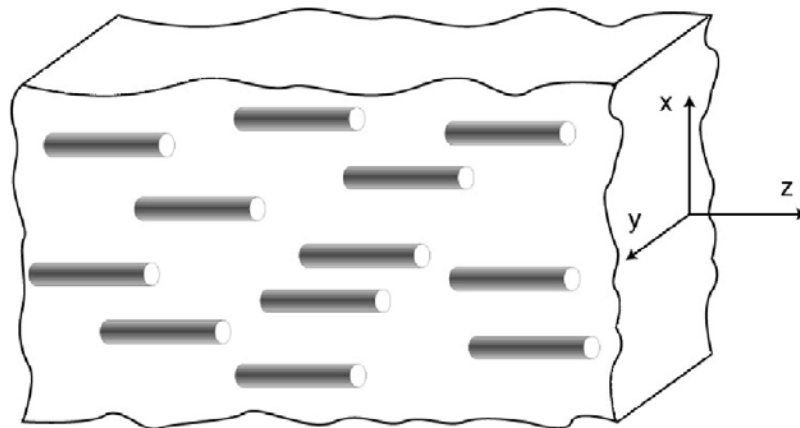
- High Strength Composites (PMCs, CMCs, MMCs...)
- Nanostructured materials: nanoparticles, powders, nanotubes...
- Multifunctional materials, self-healing materials
- Sensors (physical, chemical, bio...)
- Nanoelectromechanical systems
- Batteries, fuel cells, power systems
- Thermal barrier and wear-resistant coatings
- Avionics, satellite, communication and radar technologies
- System Integration (nano-micro-macro)
- Bottom-up assembly, impact of manufacturing

Nano-Reinforced Composites

- Processing them into various matrices follow earlier composite developments such as
 - Polymer compounding
 - Producing filled polymers
 - Assembly of laminate composites
 - Polymerizing rigid rod polymers
 -
 -
- Purpose
 - Replace existing materials where properties can be superior
 - Applications where traditionally composites were not a candidate

Benefits of Nanotechnology in Composite Development

- Nanotechnology provides new opportunities for radical changes in composite functionality
- Major benefit is to reach percolation threshold at low volumes ($< 1\%$) when mixing nanoparticles in a host matrix
- Functionalities can be added when we control the orientation of the nanoscale reinforcement.




Multifunctionality in Materials

- This always implies “structure +” since in most cases the major function of a structure is to carry load or provide shape. Additional functions can be:
- Actuation → controlling position, shape or load
- Electrical → either insulate or conduct
- Thermal → either insulate or conduct
- Health → monitor, control
- Stealth → managing electromagnetic or visible signature
- Self-healing → repair localized damage
- Sensing → physical, chemical variables

Multifunctional Materials with Sensing Capability

- Building in additional functionalities into load-bearing structures is one key example:
 - Sensing function
 - * Strain
 - * Pressure
 - * Temperature
 - * Chemical change
 - * Contaminant presence
- Miniaturized sensors can be embedded in a distributed fashion to add “smartness” or multifunctionality. This approach is ‘pre-nano’ era.
- Nanotechnology, in contrast, is expected to help in assembling materials with such functional capabilities

Examples of Multifunctional Materials

- Possible, in principle, to design any number of composites with multiple levels of functionality (3, 4, 5...) by using both multifunctional matrices and multifunctional reinforcement additives
 - Add a capsule into the matrix that contains a nanomaterial sensitive to thermal, mechanical, electrical stress; when this breaks, would indicate the area of damage
 - Another capsule can contain a healant
 - Microcellular structural foam in the matrix may be radar-absorbing, conducting or light-emitting
 - Photovoltaic military uniform also containing Kevlar for protection
 generate power during sunlight for charging the batteries of various devices in the soldier-gear

Candidates for Multifunctional Composites

- Carbon nanotubes, nanofibers
- Polymer clay nanocomposites
- Polymer cross-linked aerogels
- Biomimetic hybrids

Expectations:

- 'Designer' properties, programmable materials
- High strength, low weight
- Low failure rates
- Reduced life cycle costs

Example of Self-Healing Material

‘Self-healing plastic’ by Prof. Scott White (U. of Illinois)
Nature (Feb. 15, 2001)

- Plastic components break because of mechanical or thermal fatigue. Small cracks \Rightarrow large cracks \Rightarrow catastrophic failure. ‘Self-healing’ is a way of repairing these cracks without human intervention.
- Self-healing plastics have small capsules that release a healing agent when a crack forms. The agent travels to the crack through capillaries similar to blood flow to a wound.
- Polymerization is initiated when the agent comes into contact with a catalyst embedded in the plastic. The chemical reaction forms a polymer to repair the broken edges of the plastic. New bond is complete in an hour at room temperature.

Preparation of Nanoparticles

- Plasma processing
 - Both thermal (plasma arc, plasma torch, plasma spray) and low temperature (cold) plasma are used
- Chemical Vapor Deposition
 - Either on a substrate or in the gas phase (for bulk production)
 - Metallic oxides and carbides
- Electrodeposition
- Sol-gel processing
- Ball mill or grinding (old fashioned top-down approach)

Key Issue: Agglomeration

Desirable Attributes of Nanoparticles

Tremendous increase in surface-to-volume ratio

- Increase in solubility
- Increase in reactivity
- Possible increase in hardness (ex: titanium nitride)

Application range is wide as seen in the next two tables.

Nanoparticles

Source: Wilson et al 2002

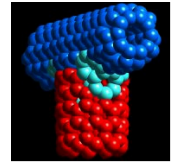
MARKET	PARTICLES REQUIRED	NANOTECHNOLOGY ADVANTAGES
Polishing Slurries	Aluminum Oxide	Faster rate of surface removal reduces operating costs
	Cerium Oxide	Less material required due to small size of particles
	Tin Oxide	Better finishing due to finer particles
Capacitors	Barium Titanate	Less material required for a given level of capacitance
	Tantalum	High capacitance due to reduction in layer thickness and increased surface area resulting from smaller particle size
	Alumina	Thinner layers possible, thus significant potential for device miniaturization
Pigments	Iron Oxide	Lower material costs, as opacity is obtained with smaller particles
	Zirconium Silicate Titanium Dioxide	Better physical-optical properties due to enhanced control over particles
Dopants	Wide variety of materials required depending on application	Improved compositional uniformity Reduction in processing temperature reduces operating and capital costs

Nanoparticles (Cont.)

Source: Wilson et al 2002

MARKET	PARTICLES REQUIRED	NANOTECHNOLOGY ADVANTAGES
Structural Ceramics	Aluminium Oxide	Improved mechanical properties Reduced production costs due to lower sintering temperatures
	Aluminium Titanate	
	Zirconium Oxide	
Catalysts	Titanium Dioxide	Increased activity due to smaller particle size
	Cerium Oxide	Increased wear resistance
	Alumina	
Hard Coatings	Tungsten Carbide	Thin coatings reduce the amount of material required
	Alumina	
Conductive Inks	Silver	Increased conductivity reduces consumption of valuable metals
	Tungsten	Lower processing temperatures
	Nickel	Allows electron lithography

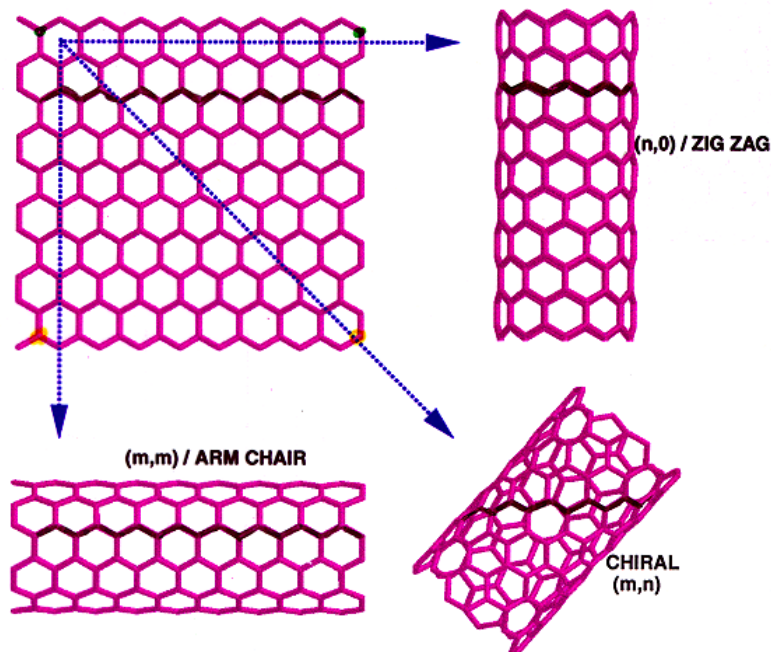
Carbon Nanotube



CNT is a tubular form of carbon with diameter as small as 1 nm.
Length: few nm to microns.

CNT is configurationally equivalent to a single or multiple two dimensional graphene sheet(s) rolled into a tube (single wall vs. multiwalled).

- STRIP OF A GRAPHENE SHEET ROLLED INTO A TUBE



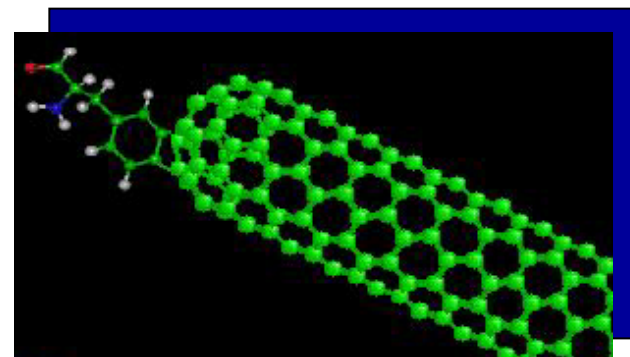
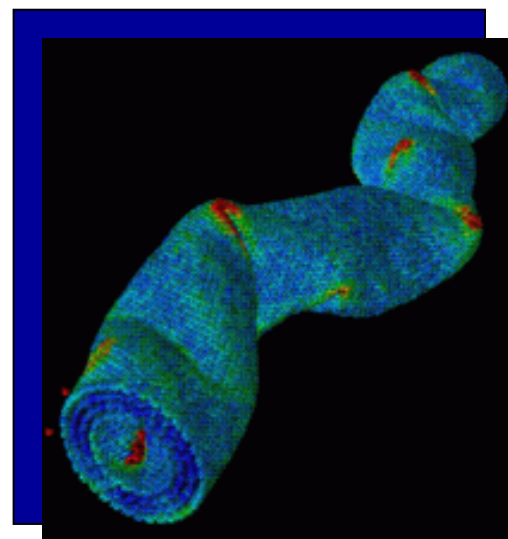
See textbook on
Carbon Nanotubes:
Science and
Applications,
M. Meyyappan,
CRC Press, 2004.

CNT exhibits extraordinary mechanical properties: Young's modulus over 1 Tera Pascal, as stiff as diamond, and tensile strength ~ 200 GPa.

CNT can be metallic or semiconducting, depending on $(m-n)/3$ is an integer (metallic) or not (semiconductor).

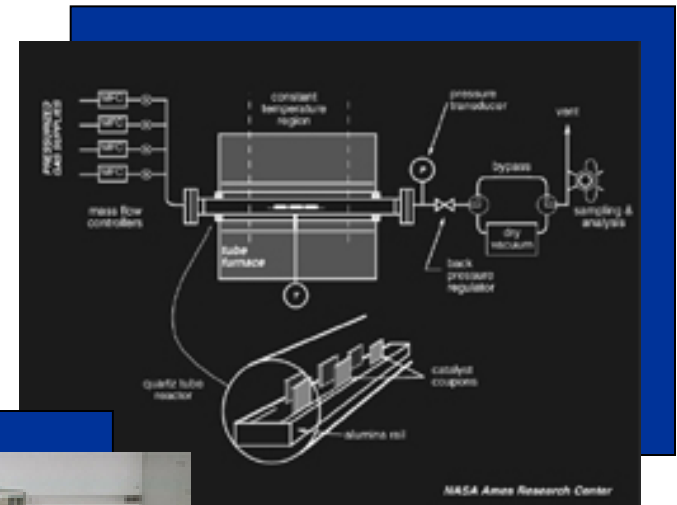
CNT Properties

- The strongest and most flexible molecular material because of C-C covalent bonding and seamless hexagonal network architecture
- Strength to weight ratio 500 times > for Al, steel, titanium; one order of magnitude improvement over graphite/epoxy
- Maximum strain ~10% much higher than any material
- Thermal conductivity ~ 3000 W/mK in the axial direction with small values in the radial direction
- Very high current carrying capacity
- Excellent field emitter; high aspect ratio and small tip radius of curvature are ideal for field emission
- Can be functionalized



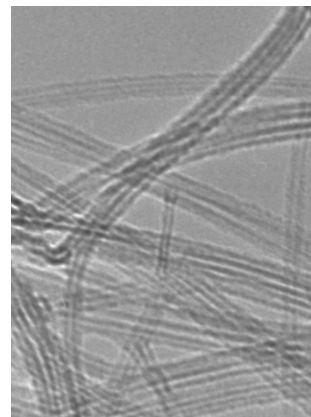
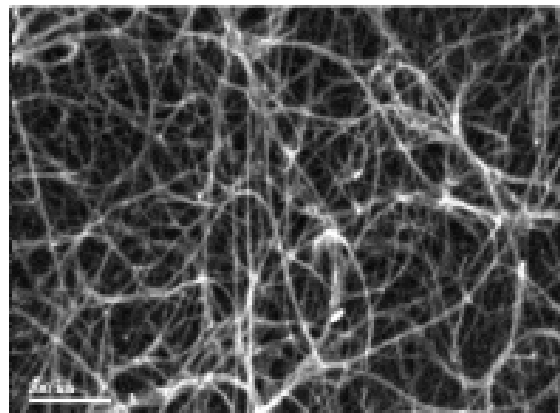
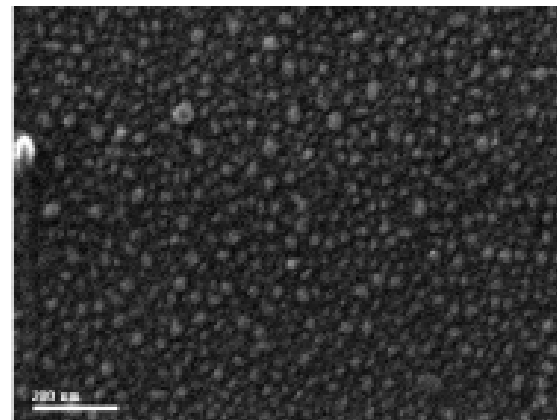
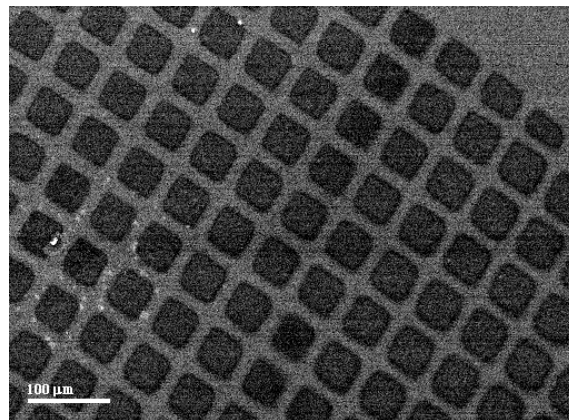
CNT Synthesis

- CNT has been grown by laser ablation (pioneered at Rice) and carbon arc process (NEC, Japan) - early 90s.
 - SWNT, high purity, purification methods
- CVD is ideal for patterned growth (electronics, sensor applications)
 - Well known technique from microelectronics
 - Hydrocarbon feedstock
 - Growth needs catalyst (transition metal)
 - Growth temperature 500-950° deg. C.
 - Numerous parameters influence CNT growth



SWNTs on Patterned Substrates

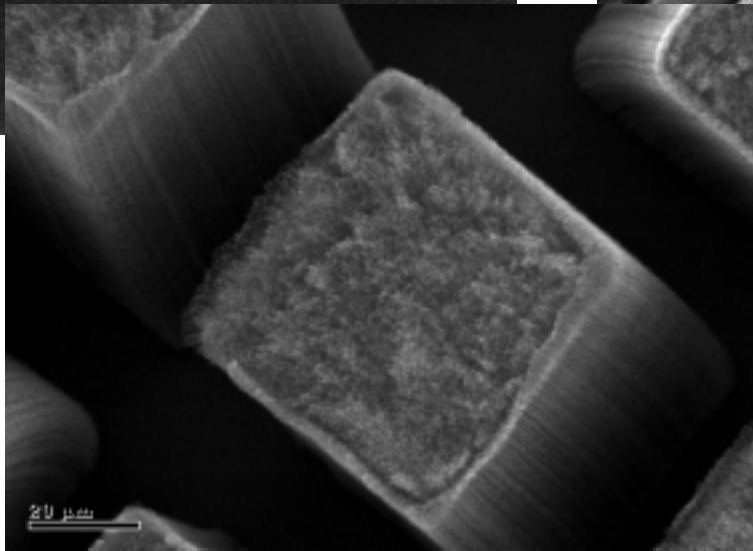
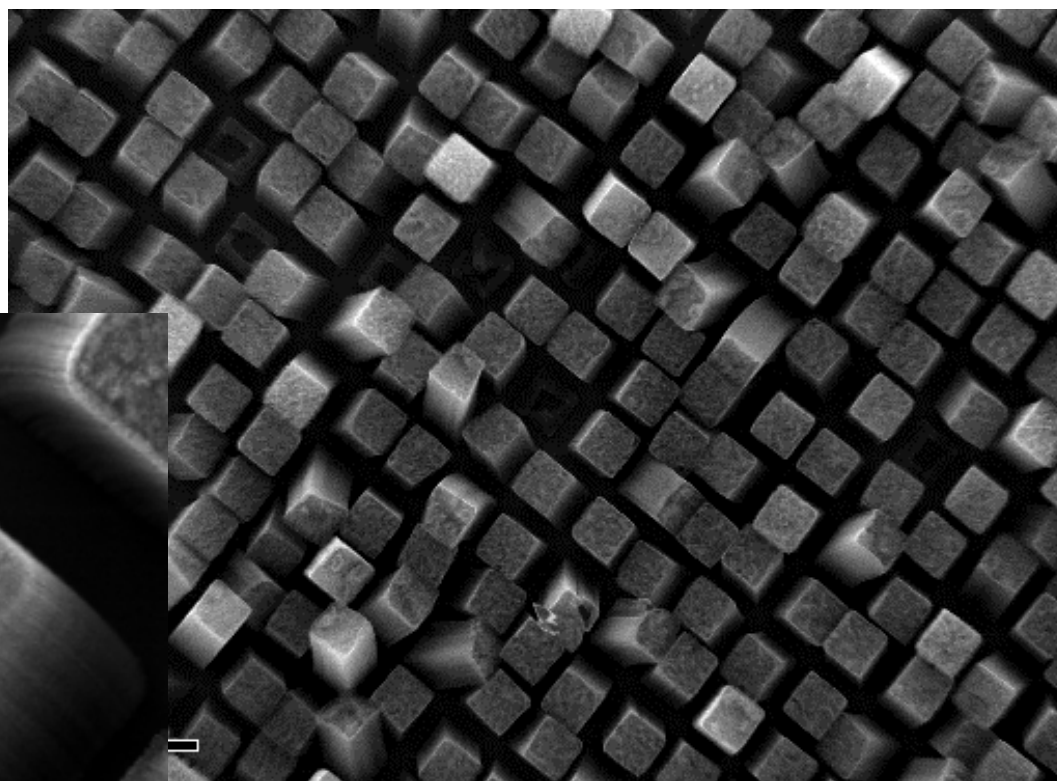
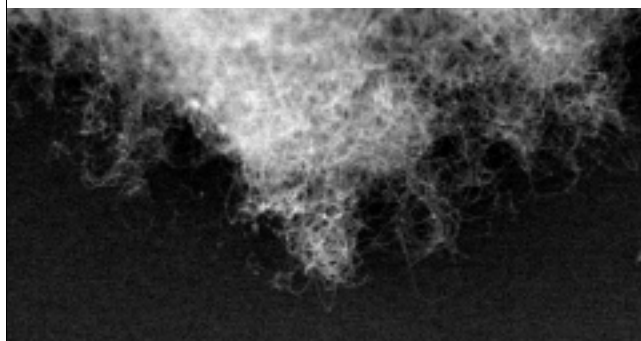
- Surface masked by a 400 mesh TEM grid
- Methane, 900° C, 10 nm Al/1.0 nm Fe



Delzeit et al., Chem. Phys. Lett.,
348, 368 (2001)

Multiwall Nanotube Towers

- Surface masked by a 400 mesh TEM grid;
20 nm Al/ 10 nm Fe; 10 minutes

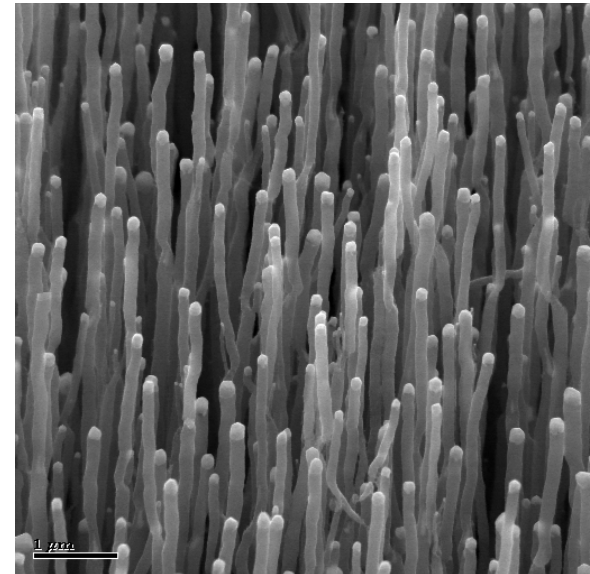


Grown using ethylene at 750° C

Plasma Reactor for CNT Growth

- Certain applications such as nanoelectrodes, biosensors would ideally require individual, freestanding, vertical (as opposed to towers or spaghetti-like) nanostructures
- The high electric field within the sheath near the substrate in a plasma reactor helps to grow such vertical structures
- dc, rf, microwave, inductive plasmas (with a biased substrate) have been used in PECVD of such nanostructures

Cassell et al., Nanotechnology, **15** (1), 2004



High Volume Production of CNTs

- Needed for composites, hydrogen storage, other applications which need bulk material
- Floating catalysts (instead of supported catalysts)
- Carbon source (CO, hydrocarbons)
- Floating catalyst source (Iron pentacarbonyl, ferrocene...)
- Typically, a carrier gas picks up the catalyst source and goes through first stage furnace ($\sim 200^{\circ}\text{C}$)
- Precursor injected directly into the 2nd stage furnace
- Decomposition of catalyst source, source gas pyrolysis, catalyzed reactions all occur in the 2nd stage
- Products: Nanotubes, catalyst particles, impurities

CNT-Based Composites

- Carbon nanotubes viewed as the “ultimate” nanofibers ever made
- Carbon fibers have been already used as reinforcement in high strength, light weight, high performance composites:
 - Expensive tennis rackets, air-craft body parts...
- Nanotubes are expected to be even better reinforcement
 - C-C covalent bonds are one of the strongest in nature
 - Young's modulus ~ 1 TPa \Rightarrow the in-plane value for defect-free graphite
- Problems
 - Creating good interface between CNTs and polymer matrix necessary for effective load transfer



WHY?

- ☆ CNTs are atomically smooth; $h/d \sim$ same as for polymer chains
- 🕒 CNTs are largely in aggregates \Rightarrow behave differently from individuals
- Solutions
 - Breakup aggregates, disperse or cross-link to avoid slippage
 - Chemical modification of the surface to obtain strong interface with surrounding polymer chains

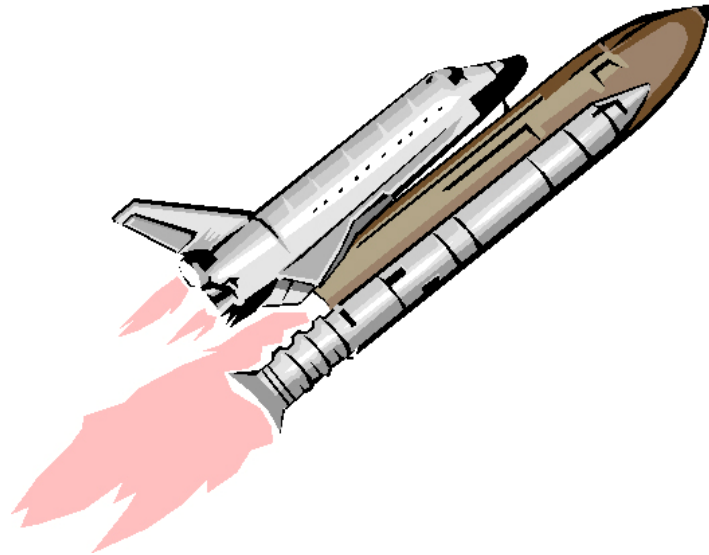
General Issues in Making CNT Composites

- Polymer matrix composites
 - Nanotube dispersion
 - Untangling
 - Alignment
 - Bonding
 - Molecular Distribution
 - Retention of neat-CNT properties
- Metal and Ceramic Matrix Composites
 - High temperature stability
 - Reactivity
 - Suitable processing techniques
 - Choice of chemistries to provide stabilization and bonding to the matrix.

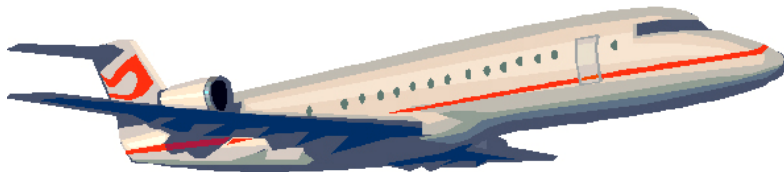
Conducting Polymers Based on Carbon Nanotubes

- High aspect ratio allows percolation at lower compositions than spherical fillers (less than 1% by weight)
- Neat polymer properties such as elongation to failure and optical transparency are not decreased.
- ESD Materials: Surface resistivity should be $10^{12} - 10^5 \Omega/\text{sq}$
 - Carpeting, floor mats, wrist straps, electronics packaging
- EMI Applications: Resistivity should be $< 10^5 \Omega/\text{sq}$
 - Cellular phone parts
 - Frequency shielding coatings for electronics
- High Conducting Materials: Weight saving replacement for metals
 - Automotive industry: body panels, bumpers (ease of painting without a conducting primer)
 - Interconnects in various systems where weight saving is critical

CNT Polymer Composites



Radiation protection
Heat dissipation coatings
Static discharge
High strength/lightweight parts
Heat engine components

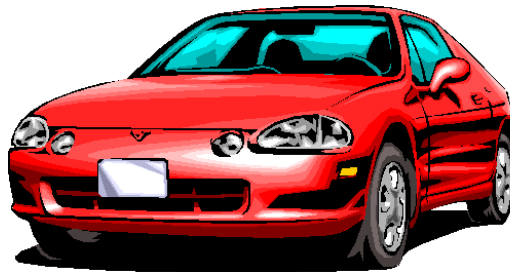


Deicing coatings
Lightning protection
Stress sensors
High strength/light weight parts
Heat engine components

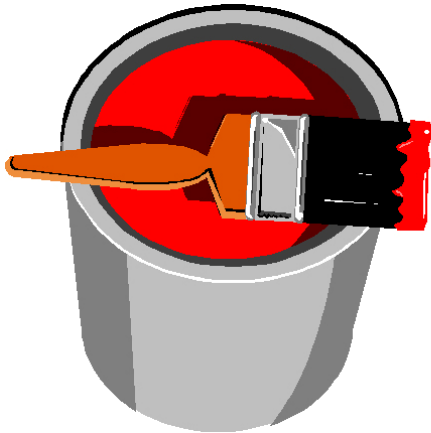
CNT Polymer Composites



Organic LEDs
High strength/light weight housings
Electrically conductive ceramics



Paintable polymers
High strength/light weight parts
Heat engine components

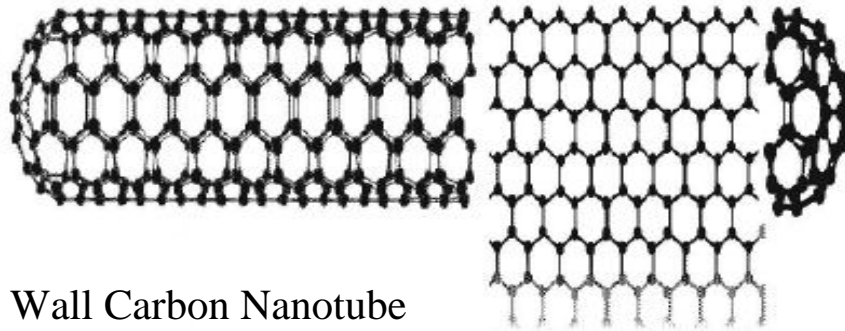


Anti-fouling paints
UV protective coatings
Corrosion protection

Nanotubes: EMI Shielding

- More & more components are packaged in smaller spaces where electromagnetic interference can become a problem
 - Ex: Digital electronics coupled with high power transmitters as in many microwave systems or even cellular phone systems
- Growing need for thin coatings which can help isolate critical components from other components of the system and external world
- Carbon nanofibers have been tested for EMI shielding; nanotubes have potential as well
 - Act as absorber/scatterer of radar and microwave radiation
 - High aspect ratio is advantageous
 - Efficiency is boosted by small diameter. Large d will have material too deep inside to affect the process. At sub-100 nm, all of the material participate in the absorption
 - Carbon fibers and nanotubes (< 2 g/cc) have better specific conductivity than metal fillers, sometimes used as radar absorbing materials.

Single-Walled Carbon Nanotubes For Chemical Sensors



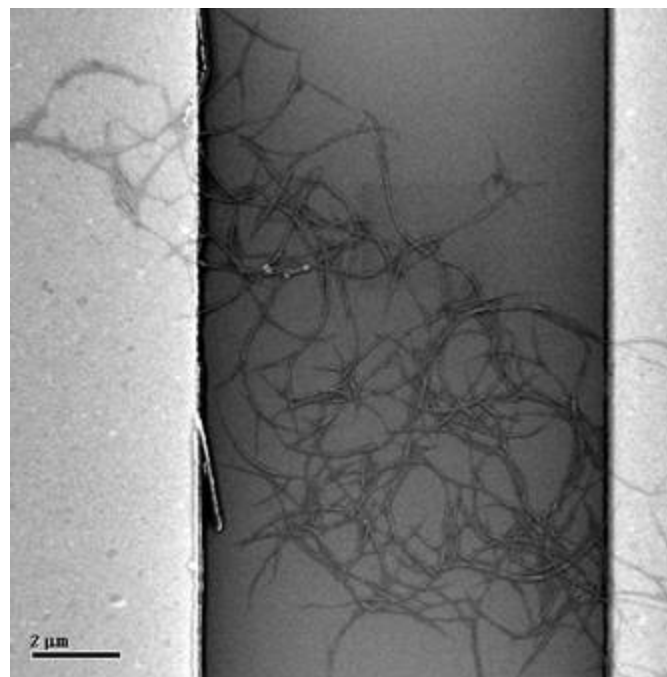
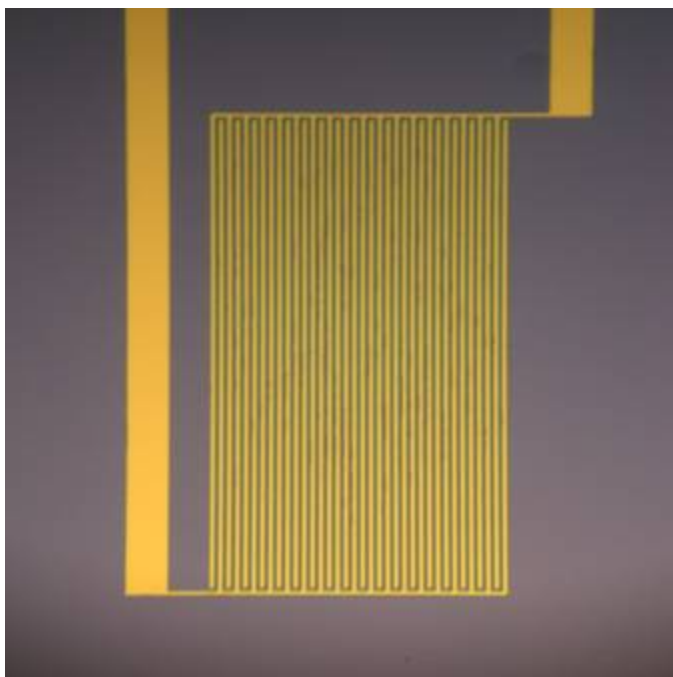
Single Wall Carbon Nanotube

- Every atom in a single-walled nanotube (SWNT) is on the surface and exposed to environment
- Charge transfer or small changes in the charge-environment of a nanotube can cause drastic changes to its electrical properties

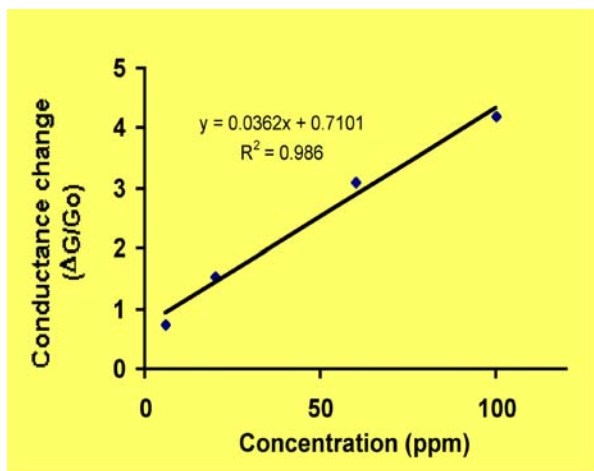
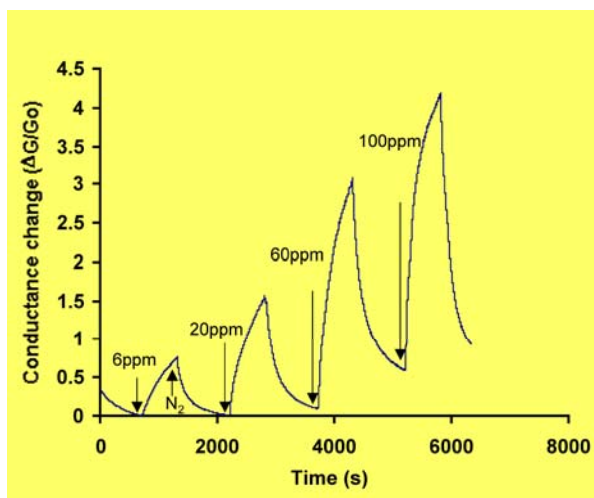
SWCNT Chemiresistor

Sensor fabrication:

1. SWCNT dispersions--Nice dispersion of CNT in DMF
2. Device fabrication--(see the interdigitated electrodes below)
3. SWCNT deposition—Casting, or in-situ growth



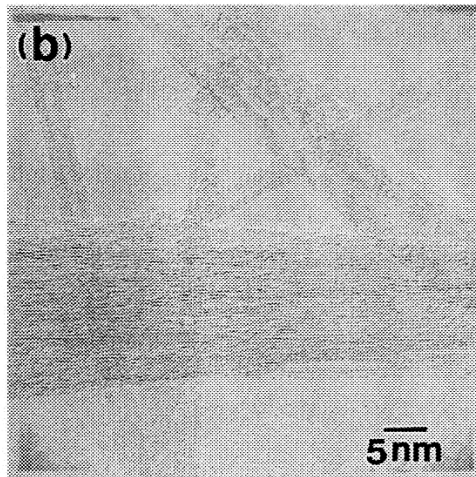
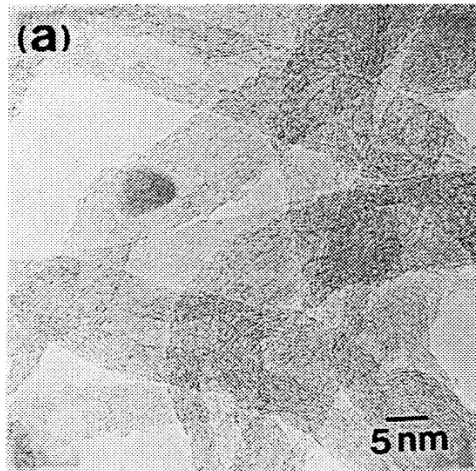
SWCNT Sensor Performance



Detection limit for NO_2 is 44 ppb.

- Sensor tested for NO_2 , NH_3 , acetone, benzene, nitrotoulene...
- Test condition:
Flow rate: 400 ml/min
Temperature: 23 °C
Purge & carrier gas: N_2
- Sensitivity in the ppb range
- Selectivity through (1) doping, (2) coating CNTs with polymers, (3) multiplexing with signal processing
- Need more work to speedup recovery to baseline

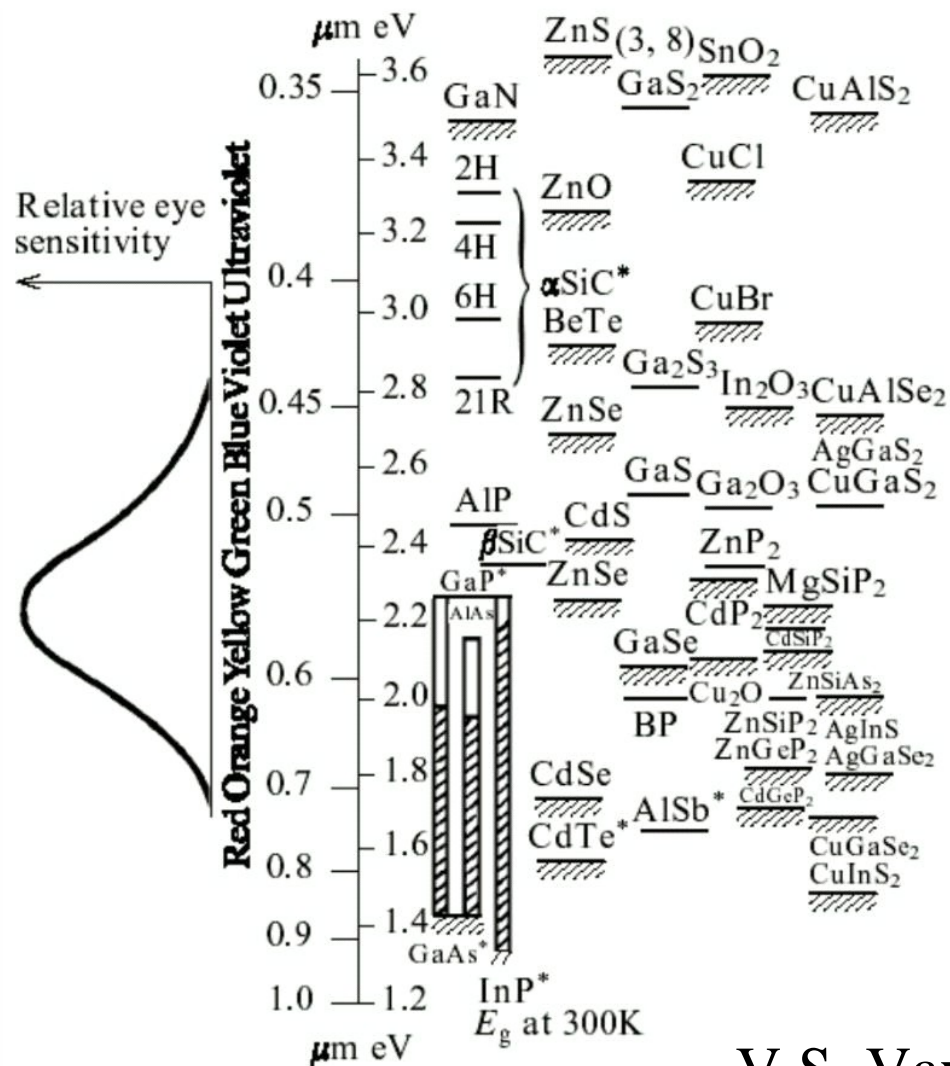
Boron Nitride Nanotubes



- Electronic properties are independent of helicity and the number of layers
- Applications: Nanoelectronic devices, composites
- Techniques: Arc discharge, laser ablation
- Also: $\text{B}_2\text{O}_3 + \text{C (CNT)} + \text{N}_2 \rightarrow 2 \text{ BN (nanotubes)} + 3 \text{ CO}$

FIG. 3. High resolution TEM images of (a) starting carbon nanotubes, and (b) boron nitride nanotubes.

Various Inorganic Nanowires (INWs)



- All these have been grown as 2-d thin films in the last three decades
- Current focus is to grow 1-d nanowires

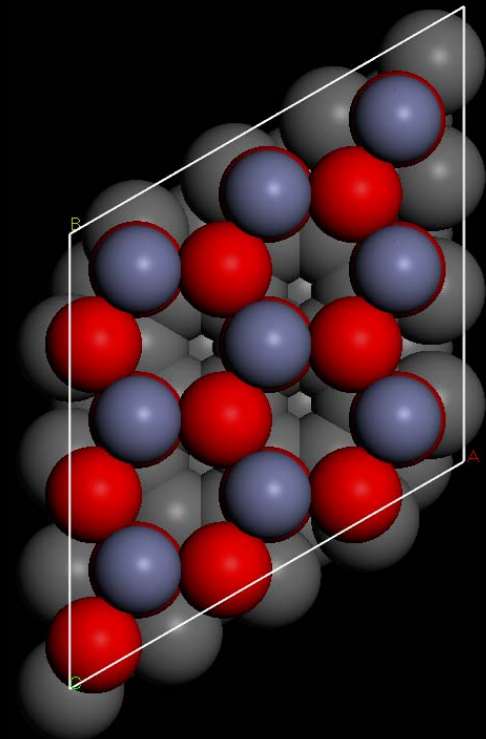
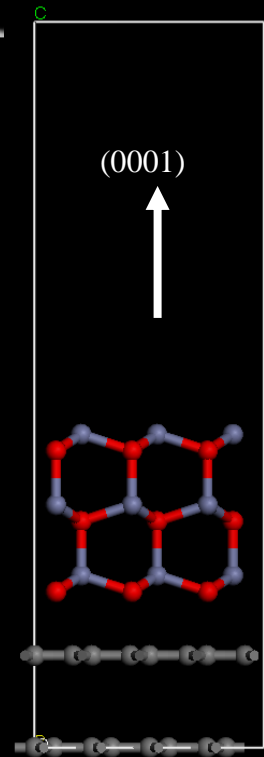
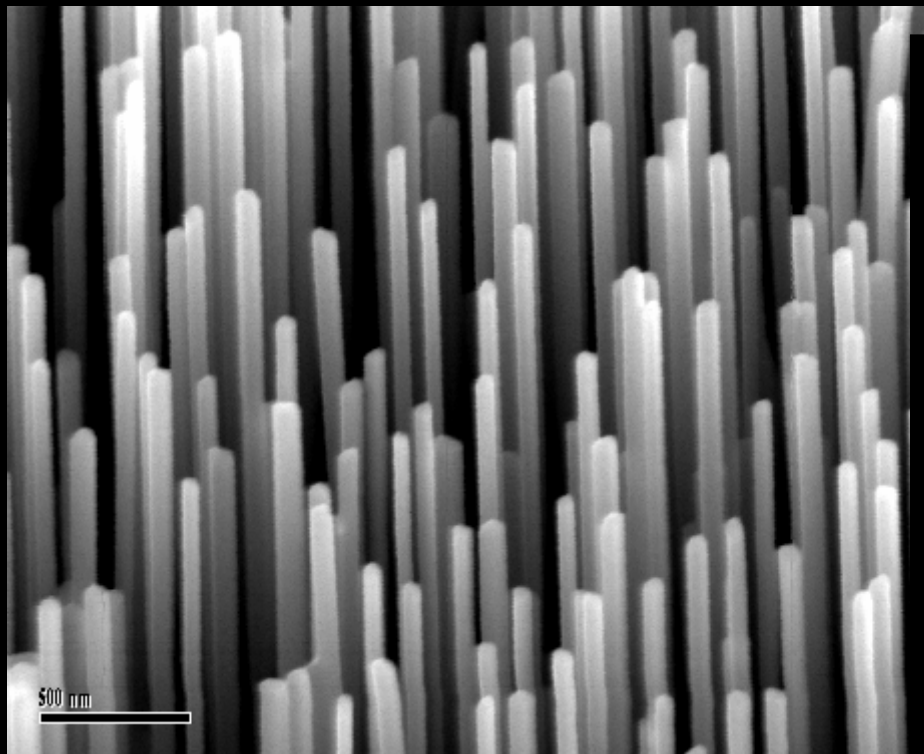
Motivation

- One-dimensional quantum confinement
- Bandgap varies with wire diameter
- Single crystal with well-defined surface structural properties
- Tunable electronic properties by doping
- Truly bottom-up integration possible

V.S. Vavilov (1994)

↓ Down to 0.4 eV

Vertically-Aligned Nanowires for Device Fabrication



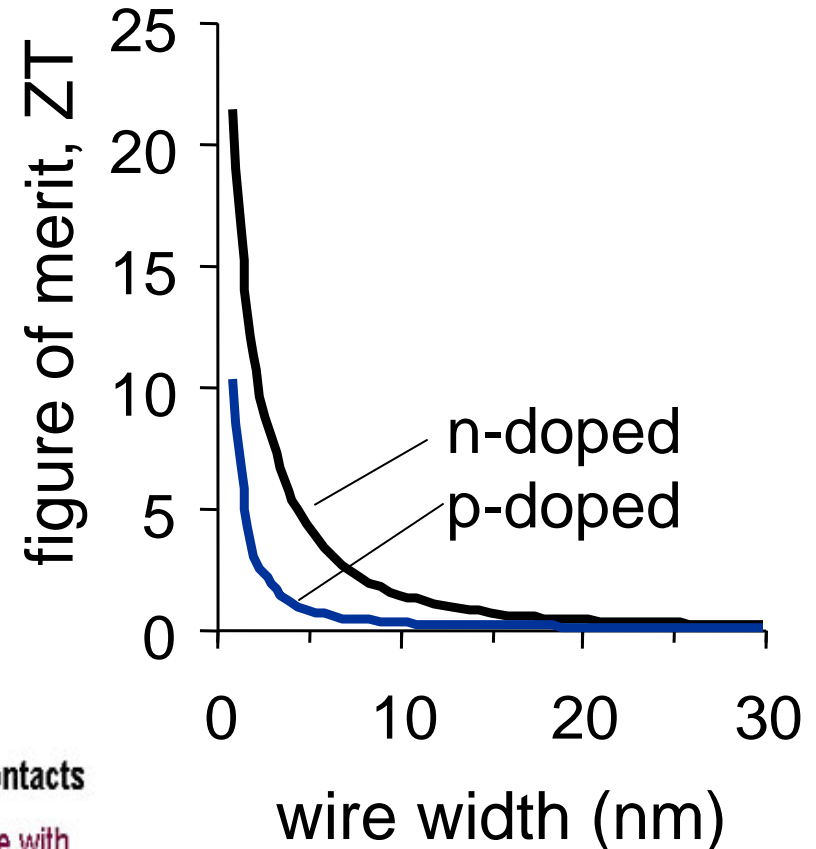
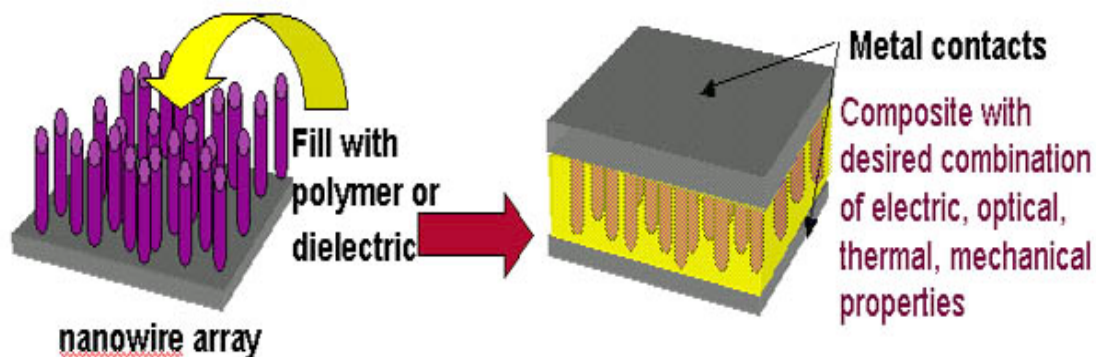
Nanowire Based Thermoelectric Element

Low dimensional systems

nanowires

- ✓ Conduction electron density of state ▼
- ✓ Seebeck coefficient ▼
- ✓ Structural constraints
thermal conductivity ➤

**PRL 47, 16631 (1993)*



Application Summary for Nanowires

MATERIAL	APPLICATION
Silicon	Electronics, sensors
Germanium	Electronics, IR detectors
Tin Oxide	Chemical sensors
Indium Oxide	Chemical sensors, biosensors
Indium Tin Oxide	Transparent conductive film in display electrodes, solar cells, organic light emitting diodes
Zinc Oxide	UV laser, field emission device, chemical sensor
Copper Oxide	Field emission device
Wide Bandgap Nitrides (GaN)	High temperature electronics, UV detectors and lasers, automotive electronics and sensors
Boron Nitride	Insulator
Indium Phosphide	Electronics, optoelectronics
Zinc Selenide	Photonics (Q-switch, blue-green laser diode, blue-UV photodetector)
Copper, Tungsten	Electrical interconnects

Summary

- Nanotechnology is an enabling technology that will impact the aerospace sector through composites, advances in electronics, sensors, instrumentation, materials, manufacturing processes, etc.
- The field is interdisciplinary but everything starts with material science. Challenges include:
 - Novel synthesis techniques
 - Characterization of nanoscale properties
 - Large scale production of materials
 - Application development
- Opportunities and rewards are great and hence, there is a tremendous worldwide interest